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Process for the production of ethylene oxide.

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Ethylene is oxidised to ethylene oxide over a silver containing catalyst which is promoted by high concentrations of potassium, rubidium or cesium, in the presence of a chlorine containing reaction inhibitor and at least 5,000 moles of ethane per mole of inhibitor expressed as its vinyl chloride equivalent. Permanent absorption of chlorine onto the catalyst (which leads to catalyst decay) is low in this process.

Process for the production of Ethylene Oxide

THIS INVENTION relates to a process for the production of ethylene oxide.

Ethylene oxide is conventionally produced by contacting ethylene and oxygen with a supported silver catalyst in the presence of a chlorine containing reaction inhibitor or modifier which is present in the gas phase. The inhibitor or modifier is normally ethylene dichloride and/or vinyl chloride and its function is to increase the selectivity of the reaction (ie to increase the number of moles of ethylene oxide produced per hundred moles of ethylene consumed). This reduces the activity of the catalyst; the reduction in activity does however reduce the danger of "hot spots" in catalyst beds.

We have found that in certain attractive catalysts chlorine is permanently absorbed from the modifier on to the catalyst bed and this gives rise to accelerated decay of the catalysts performance. We have devised conditions under which absorption of this type may be reduced to an acceptable level.

The invention comprises a process of producing ethylene oxide by contacting ethylene with oxygen in the presence of a chlorine containing reaction inhibitor and a silver containing catalyst which is promoted with potassium, rubidium and/or cesium characterised in that ethane is present in a ratio of at least 5,000, preferably at least 8,000, and more preferably at least 10,000, to 100,000 moles per mole of reaction inhibitor expressed as its vinyl chloride equivalent and that the potassium, rubidium and/or cesium content is at least 5×10^{-6} and preferably more than 8×10^{-6} and suitably at most 25×10^{-6} gram atoms per gram of catalyst in a form which is extractable by contact with dilute nitric acid.

The promoter is preferably cesium.

Chlorine containing reaction inhibitors are of different effectiveness according to their chemical structure. We have found that 0.5 moles of ethylene dichloride, 2 moles of ethyl chloride and 12 moles of

methvl chloride are equivalent to one mole of vinyl chloride. The effectiveness of other chlorine containing compounds may readily be determined empirically. By the vinyl chloride equivalent of the reaction inhibitor we mean the amount of the inhibitor necessary to produce the same inhibition as is produced by one mole of vinyl chloride.

The process is suitably carried out in a fixed bed of catalyst which may be contained in the tubes of a multi-tubular reactor. The chemical composition of the reaction inhibitor tends to change as it passes through the catalyst bed at least in part because of lay-down and removal of chlorine from the catalyst and consequently the vinyl chloride equivalent of the inhibitor may vary along the bed. If gases containing reaction inhibitor are recycled to the reactor the composition of the reaction inhibitor will tend to approach an equilibrium but if newly fed inhibitor does not correspond to that equilibrium the vinyl chloride equivalent of inhibitor may still vary along the bed. For this and other reasons it may be desirable to have catalyst with different promoter contents at the inlet and outlet ends of the bed as high levels of alkali metal tend to lead to increased permanent absorption of chlorine into the catalyst. If the reaction inhibitor is methyl chloride for example a higher alkali metal content will be desirable at the inlet end of the bed than at the outlet end of the bed because methyl chloride is comparatively ineffective as a chlorine donator, whereas if ethylene dichloride or vinyl chloride are fed as the reaction inhibitor it may be desirable to have a reduced alkali metal content at the inlet to the bed. The amounts of reaction inhibitor and ethane specified in this invention are those fed to the inlet of the catalyst bed however.

The catalyst comprises silver, suitably supported on a porous heat resisting support which may have a specific surface area in the range 0.05 to 10 m²/g preferably 1 to

5 m²/g and more preferably 1.5 to 5 m²/g as measured by the Brunauer Emmett and Teller method, the catalyst comprising the promoting amount of potassium, rubidium and/or cesium, in excess of any present in the support as
5 impurities or cements.

The silver may be introduced to a preformed porous heat resisting support as a suspension of silver or silver oxide in a liquid medium for example water or by
10 impregnation of the support with a solution of a silver compound, for example silver nitrate, which can be reduced to silver metal. If necessary a reducing agent, for example hydrogen, may be employed but a heat treatment may however suffice to decompose the silver compound to
15 silver. Suitably the impregnating solution contains a reducing agent which may be for example an anion, for example a formate, acetate, propionate, lactate, oxalate or tartarate ion, of a silver compound in the solution. The reducing agent may be for example an aldehyde, for example formaldehyde or acetaldehyde or an alcohol
20 preferably having 1 to 4 carbon atoms for example methanol or ethanol.

The solution may be a solution in water and/or an organic solvent, for example an aliphatic alcohol preferably having 1 to 4 carbon atoms; a polyhydric
25 alcohol for example ethylene glycol or glycerol; a ketone for example acetone; an ether for example dioxan or tetrahydrofuran; a carboxylic acid for example acetic acid or preferably molten lactic acid which is preferably used in the presence of water and suitably in the presence of
30 an oxidising agent for example H₂O₂; or an ester for example ethyl acetate or a nitrogen containing base for example pyridine or formamide. An organic solvent may function as a reducing agent and/or complexing agent for the silver also.

35 If the silver is introduced by impregnating a support with a solution of a decomposable silver compound it is preferred that ammonia and/or a nitrogen containing

base should be present. The nitrogen containing base suitably acts as a ligand maintaining the silver in solution; for example it may be pyridine, acetonitrile, an amine, especially a primary or secondary amine having 1-6 carbon atoms, for example isopropylamine. Other suitable nitrogen-containing bases include ammonia, hydroxylamine and alkanolamines for example ethanolamine, alkylene diamines having from 2-4 carbon atoms or polyamines containing at least three carbon atoms for example diethylenetriamine or amino ethers with at least one ether linkage and at least one primary or secondary amino group eg morpholine or amides for example formamide or dimethyl formamide. The nitrogen containing bases may be used alone or in admixture. They also act as reducing agents for the silver compound. Suitably the nitrogen containing base or bases are used together with water.

Very suitably the solution comprises silver nitrate and a primary or secondary diamine having 1 to 6 carbon atoms for example isopropylamine and water.

Alternatively the solution may be a neutral or acid solution for example it may be a solution of a silver carboxylate especially a formate, acetate, propionate, oxalate, citrate, tartarate or preferably lactate or for example a solution of silver nitrate.

The solutions preferably contain 3-50% of silver by weight.

Impregnation may be carried out in a single stage or if desired may be repeated one or more times. By this means higher silver contents of the catalyst may be achieved.

The silver compound may be decomposed for example in an atmosphere of air or preferably nitrogen.

The silver compound may generally be partially or completely reduced to silver by heating in the range 100 to 350°C, for example for a period of 5 mins to 10 hours; alternatively reduction may be carried out during the oxidation of the olefine to the olefine oxide.

The catalyst support preferably has an apparent porosity as measured by the mercury absorption method of at least 20%, for example 30-80% preferably 30-65% and more preferably 35-65% and mean pore diameters of 0.1 to 20 microns preferably 0.3 to 4 microns as measured by the mercury porosimetry method. The pore size distribution of the support may be bimodal, in which case the smaller pores preferably account for at least 70% of the total pore volume and have a mean pore diameter preferably in the range of 0.1 and preferably 0.3 to 4 microns, and the larger pores preferably have a mean pore diameter in the range 25 to 500 microns.

Most of the silver content of the catalyst is preferably present in the form of discrete particles adhering to the support having equivalent diameters of less than 10,000Å preferably in the range 20-10,000Å and more preferably 40-8,000Å for example 100-5,000Å. By equivalent diameter is meant the diameter of a hemisphere of the same silver content as the particle.

Preferably at least 80% of the silver is present as particles having equivalent diameters in the aforesaid range, the quantity of silver being judged in terms of the number of particles falling in that range. The silver is believed to be present largely as metallic silver. The dimensions of the silver particles may be determined by scanning electron microscopy.

The support may be an alumina, silicon carbide, silica, zirconia, titania or silica/alumina support, but it is preferably composed of an aggregate of alpha-alumina particles which may be fused together or cemented together with, for example silica or baryta.

The catalyst preferably comprises 3 to 50% and more preferably 3 to 30% for example 6 to 28% by weight of silver.

The potassium, rubidium or cesium may be introduced to the support before, during or after the introduction of the silver compound. Preferably it is

introduced to a support on which the silver is substantially present in metallic form. It is suitably introduced in solution in water and/or organic solvents. If it is desired to impregnate a catalyst which has
5 already been used in the oxidation of an alkene to an alkylene oxide and has lost performance, this may be carried out also.

The potassium, rubidium and/or cesium are preferably introduced as salts for example carbonates or
10 carboxylates. Polycarboxylic acids and hydroxyacids are particularly suitable. An example of a particularly suitable acid is oxalic acid.

Partial pressures of ethylene in processes according to the invention may be in the ranges 0.1 - 30
15 and preferably 1 to 30 bars. The total pressure may be in the range of from 1 to 100 and preferably 3 - 100 bars absolute. The molar ratio of oxygen to ethylene may be in the range 0.05 to 100. The partial pressure of oxygen may be in the range 0.01 and preferably 0.1 to 20 bars and
20 preferably 1-10 bars. The oxygen may be supplied for example in the form of air or preferably as commercial oxygen. A diluent for example, helium, nitrogen, argon, carbon dioxide and/or a lower paraffin other than ethane which is preferably methane may be present in proportions
25 of 10-80% and preferably 40-70% by volume in total. The amount of ethane present is suitably in the range 0.2 to 10% and preferably 0.3 to 5% by volume of the gases fed to the reaction. Suitably the diluent comprises methane as aforesaid together with, for example 2,000 to 100,000
30 and preferably 5,000 to 80,000 parts per million by total volume of ethane, preferably together with small amounts, for example 10 to 10,000 parts per million by total volume of C_3 to C_6 alkanes, cycloalkanes or alkenes preferably propylene, cyclopropane, isobutene or isobutane. It is
35 necessary to operate using gas compositions which are outside the explosive limits.

The temperature is suitably in the range 170 to

320°C, preferably 180 to 300°C and more preferably in the range 190 to 270°C. Contact times should be sufficient to convert 0.5 - 70%, for example 2 to 20 and preferably 5 - 20% of the ethylene and unconverted ethylene is, after separation of the product, suitably recycled, optionally in the presence of unconverted oxygen where appropriate and suitably after removal of CO₂.

The chlorine-containing reaction modifier may be of known type. It is preferred that it should be a C₁ to C₁₀ compound also containing hydrogen. It may be for example 1,1 or preferably 1,2-dichlorethane but it is preferred to use vinyl chloride or more preferably methyl or ethyl chloride. Chlorinated aromatic compounds, for example chlorobenzene, dichlorobenzene and chlorinated tolueⁿes are also suitable. It is preferred that the concentration of the chlorine containing reaction modifier should be at least 0.1 and more preferably at least 0.2 and at most 450, more preferably at most 10 for example at most 3 parts per million by volume expressed as its vinyl chloride equivalent.

EXAMPLE 1

The catalysts described in Examples 2 - 5 were prepared by the following method:

A solution of silver nitrate/isopropylamine complex in water was prepared by adding isopropylamine (2.2 moles) to an aqueous solution of silver nitrate (1 mole) to produce a solution containing 430 g Ag/l. The solution of the complex was used to impregnate an α -alumina support with a surface area of 2 m²/g, pore volume 0.38 cm³ g⁻¹, mean pore diameter 0.8 μ m. After soaking for 15 mins the wet support was drained for 15 mins and then transferred to a pyrolysis unit. Pyrolysis was carried out in a stream of nitrogen for two hours at 90°C, for three hours at 155°C and finally for one and a half hours at 240°C. The silver content of the finished catalyst was approximately 14% by weight.

The cesium promoter was applied by soaking the

catalyst for 15 mins in a solution of anhydrous Cs_2CO_3 in methanol (0.31 g per 100 ml). The excess solution was decanted and the wet catalyst drained for 15 mins before drying in a stream of nitrogen at 120°C for one hour.

EXAMPLE 2

Two catalysts (A and B) containing approximately 1,000 parts per million by weight of cesium were prepared as in Example 1.

10 The performance of catalysts A and B were determined as follows. 140 grams of catalyst in the form of 2 mm particles was loaded into an 11 mm internal diameter stainless steel reactor. A process gas containing 30% ethylene, 8% oxygen, 4% CO_2 , vinyl chloride, 15 ethane and the remainder nitrogen was passed over the catalyst at a gas-hourly-space-velocity of $3,760 \text{ hr}^{-1}$ and a pressure of 16 bars absolute. The reactor temperature was raised until an oxygen conversion of 40% was achieved. The catalyst selectivity at 40% oxygen conversion and the 20 temperature required to achieve 40% oxygen conversion were recorded over a period of 90 days. The performances achieved using different levels of ethane are displayed in Table 1. The catalyst tested at 2.4% ethane displayed a stable selectivity and only a slow fall in activity. That 25 tested at 0.6% ethane was initially more selective but selectivity and activity decreased rapidly with time. At this lower ethane level, catalyst A is not suitable for longer term operation at the indicated level of vinyl chloride.

Table 1

Catalyst	Vinyl Chloride (ppm by volume)	Ethane (% by volume)	Performance at Day 10		Performance at Day 90	
			S40 (%)	T40 (°C)	S40 (%)	T40 (°C)
A	3	0.6	78.4	215	76.1	232
B	3	2.4	76.3	201	76.2	207

On completion of this test the catalyst was discharged in approximately equal sections and the chloride level of each section determined using neutron activation analysis.

The results are presented in Table 2; untested samples of catalyst A and B contained less than 5 ppm chloride.

Table 2

Catalyst	Vinyl Chloride (ppm)	Ethane (% by volume)	Catalyst chloride level (ppm)	
			Front of bed	Back of bed
A	3	0.6	4100, 4900, 1200, 490, 96, 69, 72	
B	3	2.4	150, 310, 215, 115, 122, 136	

EXAMPLE 3

Two catalysts (C & D) were prepared as described in Example 1 except that the support had a surface area of $2 \text{ m}^2 \text{ g}^{-1}$, pore volume $0.3 \text{ cm}^3 \text{ g}^{-1}$ and mean pore diameter $0.6 \mu\text{m}$, and, in order to introduce 14% silver by weight silver was added in two successive similar impregnations, the impregnated catalyst being dried at 90°C for 1 hour between impregnations. In both cases the cesium promoter was added to the previously silvered support as a solution of $\text{Cs}_2 \text{CO}_3$ in methanol containing 0.32 and 0.37 g cesium/100 ml solvent respectively. Catalyst C contained

1180 ppm cesium and catalyst D contained 1250 ppm cesium by weight. The performances of catalyst C and D were determined using the same experimental procedure described in Example 2. Samples of catalyst C and D were tested in the presence of various levels of organochloro compounds and with various levels of ethane. The selectivities recorded at 40% oxygen conversion and the temperatures required to achieve 40% oxygen conversion at the end of the 14 days are presented in Table 3 together with the levels of organochloro - compound and ethane used. After each test which lasted about 14 days, samples of catalyst situated at the front, middle and back of the catalyst bed were analysed for chloride level using neutron activation analysis. These data are also shown in Table 3.

The results recorded at the end of the 14 day period show that the catalysts accumulate non uniform levels of chloride at low ratios of ethane to reaction inhibitor. The temperatures are also lower when feeding a high ratio of ethane to vinyl chloride equivalent. These tests were too short to show the selectivity changes seen in Example 2.

TABLE 3

Type of chloro compound	Level of chloro compound	Level of ethane (% by volume)	CATALYST C. 1250 ppm Cesium				CATALYST D 1180 ppm Cesium					
			S40 %	T40 °C	Chloride level after test (ppm)			S40 %	T40 °C	Chloride level after test (ppm)		
					Front	Middle	Back			Front	Middle	Back
VC	3	0.6	77.4	225	1910	950	120	76.1	220	-	-	-
VC	2	0.6	77.4	220	2350	1094	108	76.1	213	-	-	-
VC	1	0.6	77.0	210	1140	210	110	75.3	211	917	150	90
VC	3	2.4	76.0	203	150	120	140	74.7	209	1000	250	110
VC	2	2.4	75.5	201	56	80	70	75.1	206	170	107	96
VC	1	2.4	75.0	198	50	120	130	74.6	203	96	86	100
MC	10	0.6	75.9	209	164	1060	880	-	-	-	-	-
MC	6	0.6	76.1	206	-	-	-	76.3	211	84	506	443
MC	3	0.6	75.1	203	130	250	215	75.2	204	96	270	240

VC means vinyl chloride
MC means methyl chloride

EXAMPLE 4

Catalyst E to L were prepared following the method described in Example 3. The cesium promoter was added in the form of a solution of Cs_2CO_3 in methanol.

5 The cesium levels present in catalysts E to L were determined by neutron activation analysis. The results are displayed in Table 4. The performances were determined in the following way: 20 grams of catalyst in the form of 1mm particles was loaded into a stainless

10 steel reactor with an internal diameter of 8 mm. The temperature was raised in the presence of a process gas stream containing 30% ethylene, 7% oxygen with the remainder nitrogen together with ethane and vinyl chloride (VC). The gas hourly space velocity was $4,000 \text{ hr}^{-1}$

15 and the pressure was 225 psig. Different samples of catalysts E to L were tested in the presence of different levels of vinyl chloride and ethane. The levels used, together with the catalyst selectivity at 40% oxygen conversion and the temperature required to achieve 40%

20 oxygen conversion, are presented in Table 4. These performances were measured after about two weeks on line. In addition, some of these samples were analysed for chloride content using neutron activation analysis. Samples were taken from the front, middle and back of each

25 catalyst bed. These data are also displayed in Table 4. Selectivities are highest and the catalyst chloride levels more uniform at high ratios of ethane to vinyl chloride equivalent.

TABLE 4

Type of Chloride	Level of Chloride (ppm)	Level of Ethane (%)	E 250 ppm Cs		F 350 ppm Cs		G 660 ppm Cs		H 850 ppm Cs			
			S40 %	T40 °C	S40 %	T40 °C	S40 %	T40 °C	S40 %	T40 °C	Chloride level	
											Front	Middle Back
VC	3	0.6	-	-	-	-	75.9	207	78.3	192	684	206 178
VC	2	0.6	-	-	-	-	-	-	78.2	196	412	170 166
VC	1	0.6	77.3	194	77.9	190	-	-	79.1	198	216	143 160
VC	0.5	0.6	77.3	201	77.8	189	78.6	185	78.6	183	-	-
VC	2.0	2.4	-	-	77.7	194	77.8	190	78.2	190	164	161 127
VC	1.0	2.4	-	-	-	-	-	-	75.8	185	-	-

TABLE 4
contd.

Type of Chloride	Level of Chloride (ppm)	Level of Ethane (%)	I 1200 ppm Cs					J 1400 ppm Cs				
			S40 %	T40 °C	Chloride level			S40 %	T40 °C	Chloride level		
					Front	Middle	Back			Front	Middle	Back
VC	3	0.6	78.9	199	955	224	262	-	-	-	-	-
VC	2	0.6	79.6	202	890	212	189	79.5	207	1266	168	150
VC	1	0.6	79.7	205	925	147	150	78.9	200	-	-	-
VC	0.5	0.6	78.5	190	-	-	-	-	-	-	-	-
VC	2.0	2.4	79.9	195	442	179	156	-	-	-	-	-
VC	1.0	2.4	75.8	195	-	-	-	-	-	-	-	-

TABLE 4
contd.

Type of Chloride	Level of Chloride (ppm)	Level of Ethane (%)	K 1700 ppm Cs		L 2000 ppm Cs	
			S40 %	T40 °C	S40 %	T40 °C
5 VC	3	0.6	-	-	-	-
VC	2	0.6	-	-	76.0	221
VC	1	0.6	-	-	78.8	213
VC	0.5	0.6	-	-	76.7	194
VC	2.0	2.4	77.4	204	76.9	200
10 VC	1.0	2.4	-	-	-	-

EXAMPLE 5

Catalyst M was prepared using the method described in Example 3. The catalyst contained 14% (w/w) silver and 1100 ppm cesium, added as cesium carbonate in methanol.

0.4g of catalyst M tested for ethylene oxidation in the presence of a range of chlorocompounds in a stainless steel reactor 2mm in diameter and 10cm long. Catalyst M was exposed to a mixture containing 8% oxygen, 3.5% carbon dioxide, 30% ethylene, 0.6% ethane, 58% nitrogen and a low level of chlorocompound, at 225 psig pressure and a GHSV of 3000 hr⁻¹. The level of chlorocompound was adjusted until the catalyst gave an activity of 4 moles of ethylene converted per litre of reactor per hour at 40% conversion of oxygen at 200°C. The levels of chlorocompound and selectivities to ethylene oxide are shown in Table 5. The catalyst performance measured at 6ppm methyl chloride was constant over 50 days.

TABLE 5

Chlorocompound	Level ppm	Selectivity to Ethylene Oxide/%
Methyl Chloride	6.0	77.5
Ethyl Chloride	1.0	77.4
Vinyl Chloride	0.3	77.2

EXAMPLE 6

Catalysts N-R were prepared using the method described in Example 3. They contained 14% (w/w) silver and cesium loadings between 1000 and 1500 ppm added as cesium oxalate in methanol. Catalysts were tested for ethylene oxidation as described in Example 4, but with 6 ppm methyl chloride and 0.6% ethane. The performance of these catalysts are presented in Table 6.

TABLE 6

15

Catalyst	(Cesium) ppm	Selectivity at 40% Conversion/%	Temperature /°C
N	1000	78.6	195
O	1100	78.7	190
P	1200	79.1	190
Q	1300	79.2	188
R	1500	78.5	193

20

COMPARATIVE EXAMPLE

A catalyst prepared as in Example 4 was tested with vinyl chloride under the conditions described in Example 4 except that the level of vinyl chloride was 1.5 ppm. This catalyst required a temperature of 206°C to achieve 40% conversion of oxygen at a rate of 4 moles ethylene converted per litre per hour and gave a selectivity of 77.6%. Both activity and selectivity decayed with time. The discharged catalyst was analysed for chloride by neutron activation analysis. The level

30

varied from 550 ppm at the front of the bed to 320 ppm at the rear of the catalyst bed.

EXAMPLE 7

5 A silver catalyst S was prepared using the method described in Example 3. The catalyst contained 14% by weight of silver and about 800 ppm of Cs. The Cs was added as Cs_2CO_3 . 140g of catalyst S in the form of 2mm particles was loaded into a stainless steel reactor with an 11 mm internal diameter. A process gas
10 containing 30% ethylene, 8% oxygen, 4% CO_2 3-6ppm methyl chloride, 0.6% ethane and the remainder nitrogen was passed over the catalyst at a gas hourly space velocity of 3760 hr^{-1} and at a pressure of 225 psig. The performance of this catalyst was monitored over a period of 28 days. The
15 chloride level on the discharged catalyst was also determined as a function of the position in the bed using neutron activation analysis. The performances and chloride levels obtained are displayed in Table 7.

Catalyst S was then replaced in the reactor with
20 the front 20g replaced with 20g of catalyst T. Catalyst T was identical to catalyst S except that it contained 600 ppm Cs. The performance of this combination (20g catalyst T plus 120g of catalyst S) was determined over a period of 7 days, using the procedure used to test catalyst
25 S. The results are given in Table 7. Catalysts S and T were then discharged. Catalyst S was then replaced in the reactor with 20 gm of catalyst U as the front end. Catalyst U was identical to catalyst S except that it contained 1600 ppm Cs. The performance of this combination
30 (20g catalyst U plus 120g catalyst S) was determined using the same procedure over a period of 7 days. In addition the chloride level was determined as a function of bed position. The results are presented in Table 7.

TABLE 7

Catalyst		Methyl Chloride ppm	Selectivity %	Oxygen Conversion %	Temperature	Catalyst Chloride Level (ppm) (Front to back)
Front End	Back & Middle					
S	S	6	77.4	30.9	198	100, 600, 590, 508, 525
T	S	6	76.1	28.6	198	-
U	S	6	77.1	40.1	212	417, 740, 800, 765, 712

Example 8

A catalyst V was prepared as in Example 1 on an α -alumina support of surface area $1.8 \text{ m}^2/\text{g}$, pore volume $0.28 \text{ cm}^3/\text{g}$ and mean pore diameter $0.6 \mu\text{m}$. The catalyst contained 9.5% silver w/w. The catalyst was washed with distilled water at 95°C at a liquid hourly space velocity of 5 kg/kg/hr for 8 hours. Cesium was impregnated onto the catalyst from an excess of solution (1 ml solution/g catalyst) containing 0.22 g cesium oxalate/100 ml methanol/water mixture (98:2 v/v). After 16 hours immersion the catalyst was drained and dried at 120°C for 1 hour. The catalyst contained 1000 ppm cesium.

Duplicate samples of this catalyst were tested as in Example 2. 100 g of catalyst in the form of 420-1000 μm particles were charged to a stainless steel reactor with an 11 mm internal diameter. A process gas containing 30% ethylene, 8% oxygen, 4% carbon dioxide, 0.6% ethane and organochloride and the remainder nitrogen was passed over the catalyst at a gas hourly space velocity of 3760 hr^{-1} and at a pressure of 16 bars absolute. The performance of this catalyst is shown in Table 8.

Table 8

	Chloride Level (ppm by volume)	S40 /%	T40 / $^\circ\text{C}$	Test duration days	Catalyst Chloride Level (ppm)		
					Front	Middle	Back
30	VC 0.8)	30.5	214	7	106	150	145
	EC 0.8)						
	VC 2.5)	79.5	233	13	1850	328	141
	EC 2.5)						

35 VC means vinyl chloride
EC means ethyl chloride

EXAMPLE 9

A catalyst was prepared as in Example 1. Rubidium was added as its nitrate using the method described in Example 1 from a solution containing 1.5 g/l rubidium (expressed as the element). This catalyst was tested as described in Example 5. 0.4 g of catalyst were loaded into a 2 mm diameter tube, length 10 cm. A gas mixture containing 30% ethylene, 8% oxygen, 4% carbon dioxide, 1.2 ppm vinyl chloride equivalents, 0.6% ethane and the remainder being nitrogen was passed over the catalyst at 16 bars pressure absolute, and the temperature adjusted to give an activity of 4 moles of ethylene converted/kg catalyst/hr and 40% conversion of oxygen. This required a temperature of 200°C at a selectivity of 75.5%.

The levels of cesium and rubidium in the catalysts in the above Examples are the amounts extractable by contact with dilute nitric acid.

In these Examples, parts per million (ppm) and percentages in the gas phase are by volume, and parts per million and percentages in catalysts are by weight. S40 is the selectivity expressed as moles of ethylene oxide produced per 100 moles of ethylene converted at an oxygen conversion of 40% and T40 is the temperature at which this occurred. Psig means pounds per square inch gauge. GHSV means gas hourly space velocity.

Claims

1. A process of producing ethylene oxide by contacting ethylene with oxygen in the presence of a chlorine containing reaction inhibitor and a silver containing catalyst which is promoted with potassium, rubidium and/or cesium characterised in that ethane is present in a ratio of at least 5,000 moles per mole of reaction inhibitor expressed as its vinyl chloride equivalent and that the potassium, rubidium and/or cesium content is at least 5×10^{-6} gram atoms per gram of catalyst in a form which is extractable by contact with dilute nitric acid.
2. A process as claimed in Claim 1 in which at least 8,000 moles of ethane are present per mole of reaction inhibitor expressed as its vinyl chloride equivalent.
3. A process as claimed in Claim 1 or 2 in which more than 8×10^{-6} gram atoms of potassium, rubidium and/or cesium are present per gram of catalyst in a form which is extractable by contact with dilute nitric acid.
4. A process as claimed in Claim 1, 2 or 3 in which at most 100,000 moles of ethane are present per mole of reaction inhibitor expressed as its vinyl chloride equivalent.
5. A process as claimed in any preceding claim in which the promoter is cesium.
6. A process as claimed in any preceding claim in which the reaction inhibitor is ethylene dichloride or vinyl chloride.
7. A process as claimed in any preceding claim in which the catalyst comprises 3 to 30% by weight of silver supported on a porous heat resisting support which has a specific surface area of 1 to 5 square meters per gram.
8. A process as claimed in any preceding claim in which the amount of ethane present is in the range 0.3 to 5% by volume of the gases fed to the reaction.
9. A process as claimed in any preceding claim in which 0.1 to 10 parts per million by volume of reaction

inhibitor expressed as its vinyl chloride equivalent is present.

10. A process as claimed in any preceding claim in which the catalyst comprises silver supported on an alpha alumina support.



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EUROPEAN SEARCH REPORT

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Application number

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DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl. ³)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
X	<u>GB - A - 2 042 362</u> (TEXACO DEVELOPMENT CORP.) * The whole patent, and particularly page 4, lines 39-47; page 5, lines 55-65 and page 6, lines 1-25 *	1-10	C 07 D 301/10 303/04 //B 01 J 23/66
X	<u>GB - A - 2 045 636</u> (HALCON) * The whole patent *	1-10	
X	<u>GB - A - 1 563 051</u> (HALCON) * The whole patent *	1-10	
Y	<u>GB - A - 1 512 625</u> (SHELL) * The whole patent *	1-10	TECHNICAL FIELDS SEARCHED (Int.Cl. ³)
Y	<u>GB - A - 1 382 099</u> (HALCON) * The whole patent *	1-10	C 07 D 301/00 303/00
Y	<u>GB - A - 1 314 613</u> (HALCON) * The whole patent *	1-10	
Y	<u>GB - A - 1 213 483</u> (HALCON) * The whole patent *	1-10	
			CATEGORY OF CITED DOCUMENTS
			X: particularly relevant if taken alone Y: particularly relevant if combined with another document of the same category A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention E: earlier patent document, but published on, or after the filing date D: document cited in the application L: document cited for other reasons
			&: member of the same patent family, corresponding document
<input checked="" type="checkbox"/> The present search report has been drawn up for all claims			
Place of search The Hague		Date of completion of the search 01-04-1982	Examiner ALLARD

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